13 An introduction to AS Level organic chemistry

This chapter introduces organic chemistry and subsequent chapters deal with the chemistry of the organic functional groups required for AS Level. Some further general organic and functional group chemistry is revisited for A Level in Chapter 29 of this guide.

Formulae

It is important to understand and to know when to use the different ways of representing organic molecules. Read through the examples carefully so that you are in no doubt.

Molecular formula

A **molecular formula** summarises the numbers and types of atoms present in a molecule. The functional group is shown separately from the hydrocarbon chain:

$C_4H_9CH{=}CH_2$

KEY TERMS

The **molecular formula** of a compound summarises the numbers and types of atom present in a molecule.

The **structural formula** of a compound gives the minimum detail to provide an unambiguous structure.

The **displayed formula** of a compound shows the correct positioning of the atoms and the bonds between them.

The **skeletal formula** of a compound shows the carbon ‘backbone’ of a molecule, together with any functional groups.

Structural formula

A **structural formula** requires the minimum detail to provide an unambiguous structure for a compound. For example, $CH_3CH_2CH_2OH$ is acceptable for propan-1-ol, whereas C_3H_7OH is not.

Displayed formula

A **displayed formula** shows the correct positioning of the atoms and the bonds between them. For example, ethanoic acid, with the structural formula CH_3CO_2H, has the displayed formula shown in Figure 13.1.

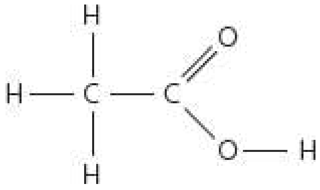


Figure 13.1 Displayed formula of ethanoic acid

You may be asked for ‘partially displayed formulae’. This means that you have to show the positions of the atoms and the bonds between them at the site of a reaction.

Skeletal formula

A **skeletal formula** is a simplified representation of an organic molecule that concentrates on the carbon ‘backbone’ of a molecule, together with any functional groups. Bonds to hydrogen atoms are *not* normally shown, unless they form part of a functional group. The skeletal formula for butan-2-ol is shown in Figure 13.2.

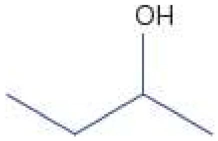


Figure 13.2 Skeletal formula of butan-2-ol

For more complex structures, where the three-dimensional structure of the molecule may be important, a ‘partial-skeletal’ formula may be used. This shows the geometry of key bonds to hydrogen (and other) atoms in the molecule, as shown in Figure 13.3.

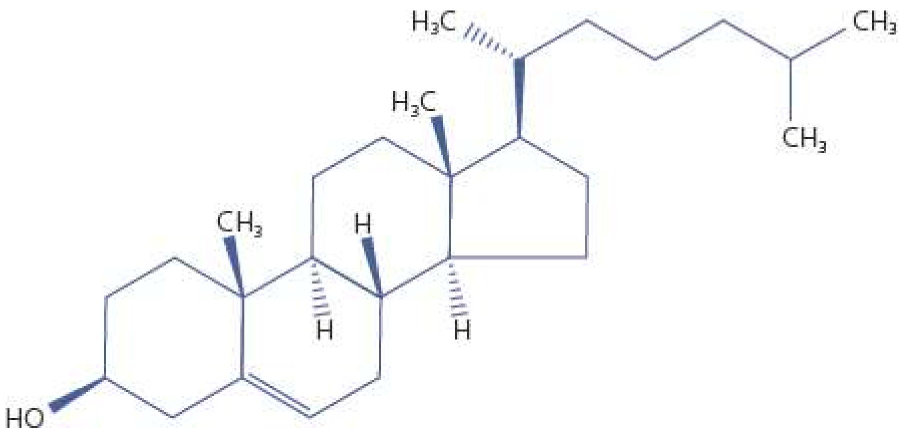


Figure 13.3 Partial skeletal formula of an organic compound (cholesterol)

Three-dimensional structures

There are times when you need to be able to show the three-dimensional structures of relatively simple molecules – for example in Figure 13.4, showing a pair of optical isomers. The convention of using a solid wedge to represent a bond coming 'out of the paper' and a dashed line for one going 'behind the paper' is used.

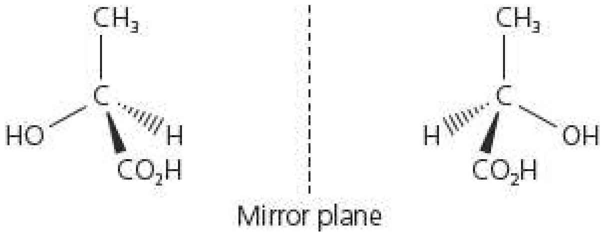


Figure 13.4 Three-dimensional structure of an organic compound

Names and functional groups

It is important that you know:

KEY TERMS

A **hydrocarbon** is a compound made up of C and H atoms only. Hydrocarbons can contain carbon–carbon single, double or triple bonds (and ring structures, as we will see in benzene (page **176**).

A **functional group** is the reactive part of an organic molecule.

- how to name **hydrocarbon** chains
- how to name the **functional groups** in organic chemistry
- how to indicate the positions of functional groups in a molecule

There are some simple rules that will help you.

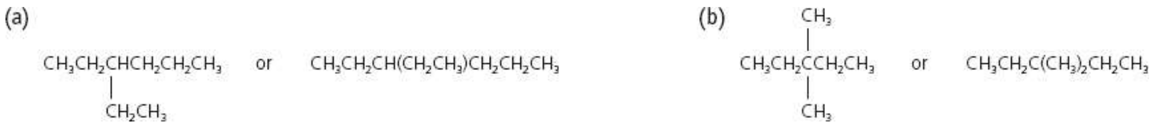
The hydrocarbon chain

The key thing to remember is that the prefix indicates the number of carbon atoms in the main chain (Table 13.1).

Table 13.1

Number of carbon atoms	Prefix used
1	meth-
2	eth-
3	prop-
4	but-
5	pent-
6	hex-
7	hept-
8	oct-

Hydrocarbon molecules do not have only straight chains – they can be branched. For a branched molecule, look at the number of carbon atoms in the branch and count the number of the carbon atom to which the branch is joined (remember to count from the end that gives the *lower* number). Some examples are shown below. Remember to use the *longest continuous* carbon chain as the basic hydrocarbon.



(a) $CH_3CH_2\underset{\substack{| \\ CH_2CH_3}}{C}HCH_2CH_2CH_3$ or $CH_3CH_2CH(CH_2CH_3)CH_2CH_2CH_3$

(b) $CH_3CH_2\overset{\substack{CH_3 \\ |}}{\underset{\substack{| \\ CH_3}}{C}}CH_2CH_3$ or $CH_3CH_2C(CH_3)_2CH_2CH_3$

Figure 13.5

So, $CH_3CH_2CH_2CH_2CH_2CH_3$ is hexane. The structures in Figure 13.5(a) are both 3-ethylhexane (an ethyl group on carbon 3) and the structures in Figure 13.5(b) are both 3,3-dimethylpentane (two methyl groups on carbon 3).

STUDY TIP

You need to be able to name simple aliphatic molecules, with the functional groups detailed in the remaining AS Level chapters on organic chemistry, with up to *six* carbon atoms (or six plus six for esters).

Alkanes

Alkanes are a family of hydrocarbons that contain only C–C single bonds and C–H bonds. Alkanes are relatively unreactive, except to combustion, and they form the major fuels that we use. All the examples given in Figures 13.5(a) and 13.5(b) are alkanes.

Alkenes

Alkenes are a family of hydrocarbons that have a reactive **functional group**, the C=C double bond. The double bond makes alkenes more reactive than alkanes and they are important organic compounds.

In alkenes, it is the position of the C=C double bond that is indicated. So, $CH_3CH_2CH{=}CHCH_2CH_3$ is called hex-3-ene and $(CH_3)_2C{=}CHCH_2CH_3$ is called 2-methylpent-2-ene (the double bond is in the second possible position and there is a methyl group branching from carbon atom 2).

Other functional groups

Some functional groups are shown in Table 13.2.

Table 13.2

Name of compound	Formula of group
Halogenoalkane/halogenoarene	–hal
Alcohol/phenol	–OH

Name of compound	Formula of group
Aldehyde	–CHO
Ketone	–C=O
Carboxylic acid	$–CO_2H$
Ester	$–CO_2R$ (where R is a hydrocarbon group)
Acyl chloride	–COCl
Amine	$–NH_2$
Nitrile	–CN
Amide	$–CONH_2$

Naming organic compounds

Naming compounds is not too difficult. Some examples are shown in Table 13.3.

Table 13.3

Formula	Name of compound
$CH_3CH_2CH_2Br$	1-bromopropane
CH_3CH_2OH	Ethanol
$CH_3CH_2CH_2CHO$	Butanal
$(CH_3)_2C=O$	Propanone
$CH_3CH_2CO_2H$	Propanoic acid
$CH_3CH_2CO_2CH_3$	Methyl propanoate
CH_3COCl	Ethanoyl chloride
$CH_3CH_2CH_2CH_2NH_2$	1-aminobutane

Formula	**Name of compound**
$CH_3CH_2CH_2CN$	Propanenitrile
CH_3CONH_2	Ethanamide

NOW TEST YOURSELF

1 What is the name of the compound shown in Figure 13.4?

2 Name these compounds:

  a $CH_3CH_2CH_2CH_2Cl$

  c $CH_3CH_2CH_2CH_2CH_2CO_2H$

  b $CH_3CHOHCH_3$

  d $CH_3CH(CH_3)CH_2CH_2NH_2$

3 Draw structural formulae for these compounds:

  a 2-bromobutane

  c methanal

  b propanamide

  d methyl ethanoate

Organic reactions

It is important to be able to remember, and in some cases to predict, what types of reaction a compound containing a particular functional group will take part in. To do this you need to be aware of both the nature of the functional group and the possible reactions a given reagent may allow.

Fission of bonds

Organic molecules are held together by covalent bonds, so you no longer need to worry about ionic reactions (except in a few rare cases). In organic molecules, a given bond can split in two ways.

- In homolytic fission (Figure 13.6) one electron goes to each fragment:

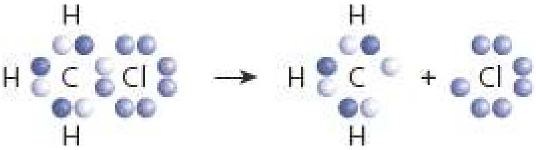


Figure 13.6 Homolytic fission

KEY TERM

In **homolytic fission** the bond splits so that one electron goes to each fragment.

- In **heterolytic fission** (Figure 13.7) both electrons go to one fragment and none to the other:

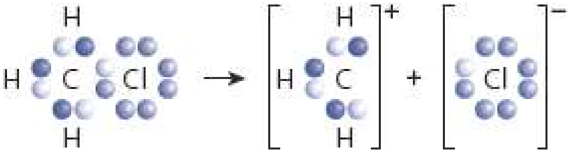


Figure 13.7 Heterolytic fission

KEY TERM

In **heterolytic fission** both electrons go to one fragment and none to the other.

Free radical reactions

Free radicals are highly reactive species having at least one unpaired electron. In equations, it is usual to show the unpaired electron as a dot. These free radicals may be formed by the action of ultraviolet light (such as in the Earth's upper atmosphere) or by the breakdown of a very unstable organic compound.

In general, free radical reactions take place in three distinct steps – **initiation**, **propagation** and **termination**.

KEY TERMS

Free radicals are usually highly reactive species consisting of an atom or fragment of a molecule with an unpaired electron.

Initiation is the first stage in a free radical reaction, in which the free radicals are formed.

Step 1: initiation

The reaction you will study is the reaction of methane with chlorine in the presence of ultraviolet light.

Free radicals are formed by the breaking of bonds by homolytic fission:

$$Cl{-}Cl \rightarrow Cl\bullet + Cl\bullet$$

Step 2: propagation

The free radicals formed begin a chain reaction in which each free radical is used to form another:

$$H{-}CH_3 + Cl\bullet \rightarrow CH_3\bullet + HCl$$

$$CH_3\bullet + Cl{-}Cl \rightarrow CH_3Cl + Cl\bullet$$

Step 3: termination

These are reactions in which free radicals combine and hence end that part of the chain reaction:

$$Cl\bullet + Cl\bullet \rightarrow Cl_2$$

$$CH_3\bullet + Cl\bullet \rightarrow CH_3Cl$$

$$CH_3\bullet + CH_3\bullet \rightarrow CH_3CH_3$$

KEY TERMS

Propagation is the second stage in a free radical reaction. In this, for each free radical used, a new one is formed.

Termination is the final stage in a free radical reaction. In this, free radicals combine together, removing them from the reaction.

Nucleophilic and electrophilic reactions

Nucleophilic reagents ‘like’ positive charges and electrophilic reagents ‘like’ areas of relatively high electron density.

STUDY TIP

A way to remember this is ‘nucleo like nucleus, which is positive; electro like electrons, which are negative’. It follows that the reagents themselves are the opposite of what they seek.

Nucleophiles

Nucleophiles include halide ions, hydroxide ions, cyanide ions and molecules having lone pairs of electrons, such as water and ammonia, or even ethanol. A typical nucleophilic substitution reaction is:

$$CH_3CH_2CH_2Br + OH^- \rightarrow CH_3CH_2CH_2OH + Br^-$$

Electrophiles

Electrophiles are electron-deficient species – generally positively charged ions such as H^+, Cl^+, Br^+, I^+, NO_2^+, CH_3^+, CH_3CO^+. An example of an electrophilic addition reaction is:

$$CH_3CH{=}CH_2 + HBr \rightarrow CH_3CHBrCH_3$$

KEY TERMS

A **nucleophile** is a negatively charged ion or a molecule with lone pairs of electrons, which can attack positive centres in organic molecules.

An **electrophile** is a positively charged ion, which can attack negative centres in organic molecules.

NOW TEST YOURSELF

4 Why can water act as a nucleophile in organic reactions?

Other types of reaction

Addition

Addition refers to an increase in saturation, in other words adding a molecule to a C=C double bond as in the above reaction. The molecule achieves this by interacting with the π-electrons in the double bond (see the section on the structure of ethene on page 86).

Substitution

Substitution refers to the replacement of one group in an organic molecule by another, as in nucleophilic substitution above. Both nucleophiles and electrophiles can take part in substitution reactions.

Elimination

An **elimination** reaction involves the removal of atoms from two adjacent carbon atoms to leave a double bond. It is the reverse of the electrophilic addition reaction above.

Hydrolysis

Hydrolysis is a reaction, usually in aqueous solution, between organic molecules and water, or acid or alkali, that leads to the formation of at least two products. Two examples are:

$$(CH_3)_3C{-}Cl + 2H_2O \rightarrow (CH_3)_3C{-}OH + H_3O^+ + Cl^-$$

$$CH_3CO_2CH_3 + NaOH \rightarrow CH_3CO_2^-Na^+ + CH_3OH$$

Condensation

A **condensation** reaction is the reverse of hydrolysis. Water is eliminated when two organic molecules react together. An example of this is the reaction of an alcohol with a carboxylic acid to form an ester:

$$CH_3CO_2H + CH_3OH \rightarrow CH_3CO_2CH_3 + H_2O$$

It is also the reaction by which an important group of polymers is made (see page 201).

Oxidation

In general, this refers to the **oxidation** of a C–OH group to form a C=O group in an aldehyde, ketone or carboxylic acid. Such oxidations are often brought about by warming the organic compound with acidified potassium dichromate(VI). This can produce complicated equations, and it is permissible to show the oxidising agent as [O]:

$$CH_3CH_2OH + [O] \rightarrow CH_3CHO + H_2O$$

Reduction

This is the opposite of oxidation and, in general, applies to compounds containing a C=O group. **Reduction** can be brought about by several reducing agents, including tin and dilute hydrochloric acid, sodium in ethanol and lithium aluminium hydride. In organic reduction reactions, the reducing agent is usually represented by [H]:

$$CH_3CO_2H + 4[H] \rightarrow CH_3CH_2OH + H_2O$$

NOW TEST YOURSELF

5 A condensation reaction can be thought of as the reverse of hydrolysis. Explain why.

Shapes of molecules

For AS Level, you need to know the shapes of ethane and ethane molecules. For A Level, you also need to know the shape of a benzene molecule. Alongside this, you must be able to work out the shapes of related molecules. The basics of this were covered in Chapter 3 – here are some reminders.

Ethane

An ethane molecule is formed (Figure 13.8) by electrons in hydrogen 1s-orbitals overlapping with electrons in $2sp^3$-orbitals on the carbon atoms to form molecular orbitals in which the hydrogen nuclei are embedded.

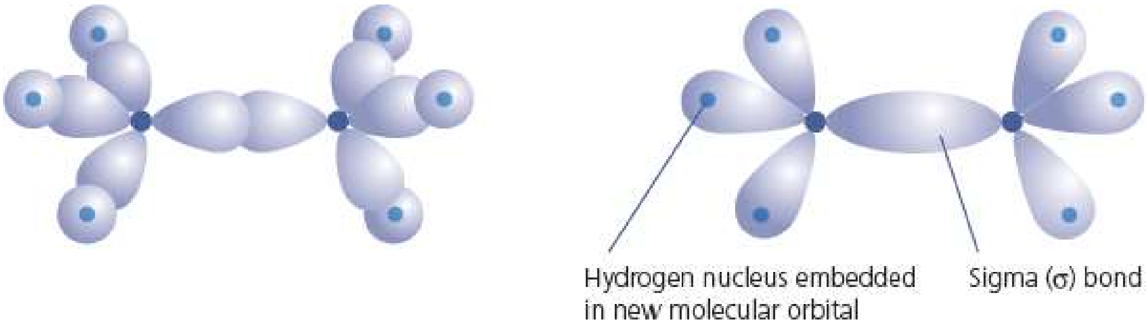


Figure 13.8

STUDY TIP

Arenes are important for A Level. For AS Level you need to be able to recognise the benzene ring, even though you do not need to know anything about benzene or its compounds.

A single C–C σ-bond, formed by the overlapping of one sp^3-orbital from each carbon atom, joins the two ends together but there is no restriction on rotation so the two ends of the molecule can spin relatively freely.

Ethene

In ethene, the carbon atoms form $2sp^2$-hybrid orbitals using three of the electrons, leaving one electron in a 2p-orbital (Figure 13.9).

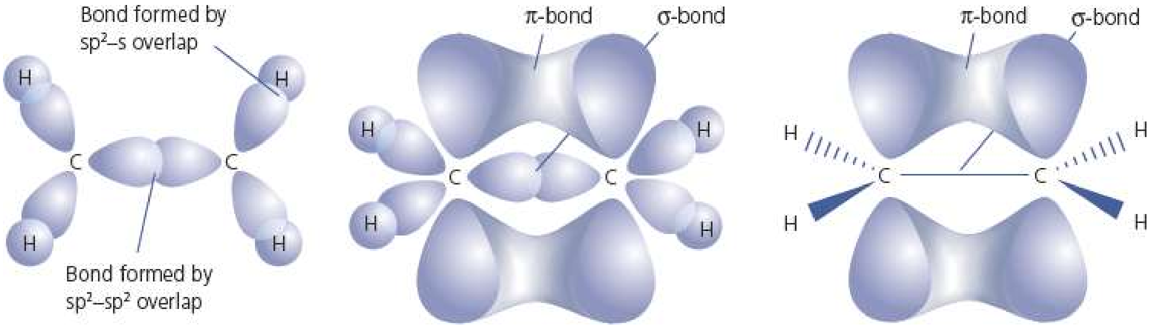


Figure 13.9

An ethene molecule is formed by the overlap of two sp^2-orbitals on each carbon atom with two hydrogen 1s-orbitals. The third sp^2-orbitals on each carbon atom overlap to form a σ-bond. The p-orbitals interact to form an additional π-bond, which prevents the rotation of the ends of the molecule about the σ-bond.

NOW TEST YOURSELF

6 Ethane has a three-dimensional structure, but the atoms in ethene all lie in the same two-dimensional plane. Explain why.

Isomerism

Isomers are compounds that have the same molecular formula (same chemical composition) but different structural formulae. You need to know about three main types of isomerism – structural, geometrical and optical.

Structural isomerism

Chain isomerism

In **chain isomerism**, the isomers arise due to branching of the carbon chain. So C_4H_{10} can have both a straight-chain form and a branched-chain form (Figure 13.10).

KEY TERM

Chain isomerism arises due to branching of the carbon chain.

Figure 13.10

The compounds have different names based on the system described on page 81. The branched chain is three carbon atoms long and has a methyl group on the second carbon atom.

Position isomerism

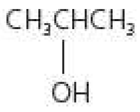
In **position isomerism**, the carbon chain is fixed, but the position of substituent groups can vary. The alcohols propan-1-ol and propan-2-ol show this (Figure 13.11).

KEY TERM

Position isomerism arises due to variation in the position of substituent groups on the carbon chain.

$CH_3CH_2CH_2OH$

Propan-1-ol



$$\underset{\displaystyle OH}{CH_3\overset{}{C}HCH_3}$$

Propan-2-ol

Figure 13.11

Changing the position of a group can affect how readily the compound reacts, as well as its physical properties such as boiling point. Propan-1-ol has a boiling point of 97°C whereas propan-2-ol has a boiling point of 82°C.

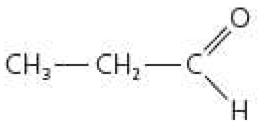
Functional group isomerism

In **functional group isomerism**, the nature of the functional group in the molecules is different. This is significant because it changes the chemical reactions that the molecules undergo. The formula C_3H_6O can represent any of the three molecules in Figure 13.12, each with a different functional group:

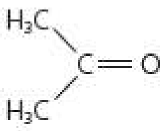
KEY TERMS

Functional group isomerism arises because rearrangement of the atoms in the molecule means that the nature of the functional groups are different in the isomers.

Geometric isomerism occurs when there is restricted rotation around a bond, such as in alkenes.



Propanal



Propanone

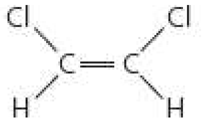
$CH_2{=}CH—CH_2—OH$

2-propen-1-ol

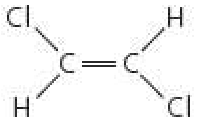
Figure 13.12

Geometric (*cis–trans*) isomerism

Geometric isomerism occurs when there is restricted rotation around a bond, such as in alkenes. It also needs two groups, one on each end of the double bond, such as in 1,2-dichloroethene.

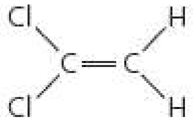


Cis-1,2-dichloroethene



Trans-1,2-dichloroethene

Figure 13.13



1,1-dichloroethene

Figure 13.14

The two forms in Figure 13.13 are different because the double bond prevents the rotation needed to make the two forms identical. Note that there is another isomer (Figure 13.14), but this one is a position isomer rather than a *cis–trans* isomer.

To summarise, in *cis–trans* isomerism:

- There is restricted rotation, generally involving a carbon–carbon double bond.
- There are two different groups on the left-hand end of the bond and two different groups on the right-hand end.

Optical isomerism and chiral centres

- The final type of isomerism you need to be able to recognise and explain is **optical isomerism**, which is another form of stereoisomerism. This gets its name from the effect an optical isomer has on the plane of plane-polarised light.
- One isomer rotates polarised light clockwise, and the other isomer rotates it an equal amount anticlockwise. This occurs when there is a carbon atom

with four different groups attached to it – this is called a **chiral** carbon.

- An example was shown on page **81** and another example, butan-2-ol, is shown in Figure 13.15.

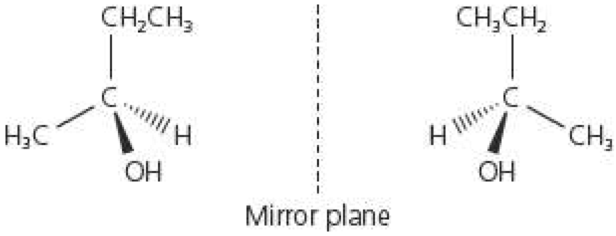


Figure 13.15

KEY TERM

A **chiral** carbon atom is one with four different groups attached to it.

- Notice that the two molecules in Figure 13.15 are mirror images, and that the central carbon atom has four different groups attached.

STUDY TIP

Check that your diagrams make chemical 'sense'. Take the structure of 2-aminopropanoic acid in Figure 13.16 for example. It is important to show the acid group joined to the central carbon the right way round. (If not, you may be penalised in the exam.) Figure 13.16 shows what you need to do.

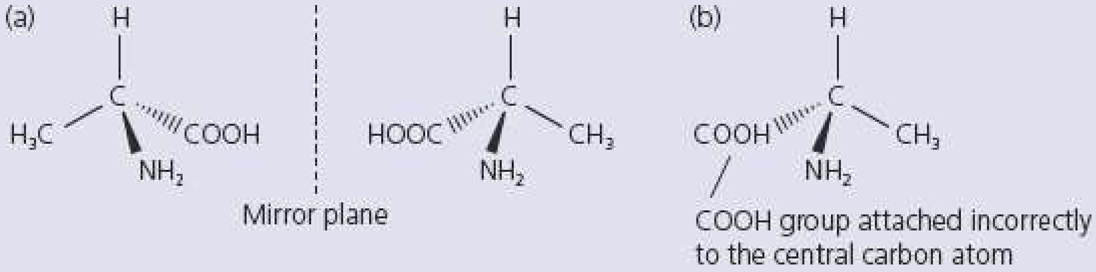


Figure 13.16 (a) Optical isomers of 2-aminopropanoic acid. (b) Incorrectly drawn isomer

Identifying chiral carbon atoms can be tricky, particularly in complex or skeletal molecular structures. You have to work out whether or not a given carbon atom has two (or more) identical groups attached to it.

Look at the skeletal structure in Figure 13.17:

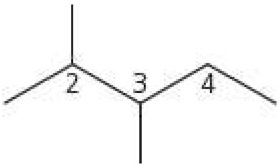


Figure 13.17

- It contains three non-terminal carbon atoms, numbered 2, 3 and 4.
- Look at each of these in turn. Carbon-2 has two bonds attached to methyl groups, carbon-4 has two bonds attached to hydrogen atoms (not shown), and carbon-3 is attached to four different groups. Therefore, carbon-3 is chiral.
- You may be asked to examine a complex molecule and state the number of chiral carbon atoms (or perhaps circle them). An example of such a molecule, the synthetic form of the hormone testosterone, is shown in Figure 13.18. Can you identify the chiral carbon atoms in the structure? There are six.

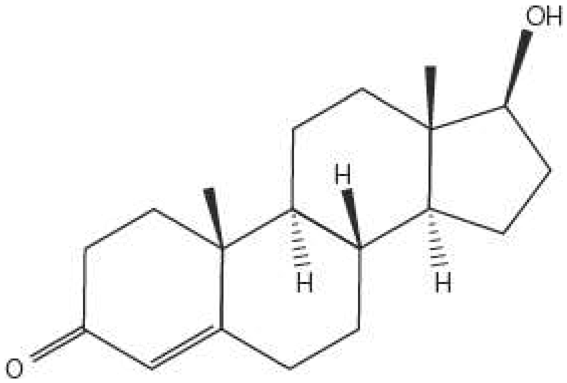


Figure 13.18 Synthetic testosterone

NOW TEST YOURSELF

7 Compound P has the molecular formula C_3H_6O.

a Draw a structure for P that is a carbonyl compound.

b Does P have functional group isomers? If so, draw examples.

c How many isomers in total does the straight-chain form of P have, incorporating any of the functional groups in Table 13.2?

8 Compound Q has the formula C_3H_5Cl and contains a double bond.

a How many non-cyclic isomers exist for Q?

b Draw the *cis–trans* isomers of Q.

REVISION ACTIVITY

a Draw the structures for the following compounds:

- **i** 3-ethylpentane
- **ii** 4-methylheptane
- **iii** 3-heptene

b Draw all the chain isomers of butene. Which of these are *cis–trans* isomers?

c What is the difference between an electrophilic reagent and a nucleophilic reagent?

d An alkane cannot undergo addition reactions. Explain why.

END OF CHAPTER CHECK

By now you should be able to:

- define the term hydrocarbon
- understand that alkanes contain no functional group but that the properties of organic compounds are dictated by the functional group they contain
- interpret and use general, structural, displayed and skeletal formulae
- understand and use systematic nomenclature of simple aliphatic compounds containing up to six carbon atoms
- deduce the molecular and/or empirical formula of a compound from its structural, displayed or skeletal formula
- interpret and use terminology associated with types of organic compounds and reactions
- describe the shapes of organic molecules as straight-chained, branched or cyclic; describe the arrangement of σ and π bonds in

molecules

- describe structural and stereoisomerism (*cis*–*trans* and optical); explain what is meant by a chiral centre and identify this in a molecule
- deduce possible isomers for a given organic molecule